Changes of dissolved oxygen during the caffeine oxidation by photo-Fenton

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Abstract
The aim of this work is to analyse the changes of dissolved oxygen ([DO], mg/L) during the oxidation of caffeine waters by photo-Fenton treatment. The concentration of dosed hydrogen peroxide would be the addition of the stoichiometric $[H_2O_2]$, which reacts with organic matter ($[H_2O_2]_{esteq}$=2.0 mM), plus the concentration in excess of $[H_2O_2]_{exc}$ that decomposes, generating O_2 through radical processes, according to a ratio R=0.8164 mmol H_2O_2/mg O_2). Operating at doses lower than the stoichiometric value $[H_2O_2]_0$<2.0 mM, O_2 is not emitted, as there is no excessive oxidant. Besides, it is verified that the Fe^{2+} ion is oxidized to Fe^{3+}, with subsequent regeneration to Fe^{2+}. Applying higher doses than the stoichiometric [$[H_2O_2]_0$>2.0 mM, oxygen is released, and regeneration of Fe^{3+} to Fe^{2+} does not occur. The highest oxygen generation output is obtained when dosing $[Fe]_0$=10.0 mg/L, conducting at pH=3.0 and 25ºC. The evolution of DO formation is adjusted to zero-order kinetics, the kinetic constant of oxygen generation being k_f=29.48 $[Fe]_0^{-1.25}$ (mg O_2 L^{-1} min^{-1}) and oxygen consumption k_d=-0.006 $[Fe]_0^{2.0}$ + 0.244 $[Fe]_0^{-3.7}$ (mg O_2 L^{-1} min^{-1}).
Keywords: caffeine; dissolved oxygen; ferrous ion; kinetic modelling; photo-Fenton

1. Introduction

Currently, more than 40,000 organic compounds are detected within the so-called "contaminants of emerging concern", which can cause toxic effects on human health and serious risks for the ecological environment (Sun et al., 2018). Since the European Water Framework Directive (2000/60/CE) aims to ensure the quality of surface and subterranean waters, environmental quality standards are established. They include up to 45 priority groups of substances that represent a significant risk to the aquatic environment and human health (Directive 2013/39/UE). Following this regulation, the EU Supervisory List of Control of Potentially Harmful Substances was approved (Decision 2015/495/CE), (Vystavna et al., 2018). The main concern is that conventional wastewater treatment plants (WWTPs) are not designed to eliminate these pollutants, as their concentrations are of the order of ng/L or μg/L (Martín et al., 2018).

Caffeine (1,3,7-trimethylxanthine $C_8H_{10}N_4O_2$) is a methylxanthine alkaloid classified as emerging contaminant. Around 5% of the ingested caffeine is not metabolized, but excreted in the urine and discharged in the water in concentrations that vary between 0.001 μg/L and 753 μg/L (Montagner et al., 2014). Nevertheless, its effects on human health and the environment are not yet evaluated properly. Therefore, it is necessary to implement effective processes to reducing these contaminants (Villota et al., 2018).

2. Materials and Methods

Samples of caffeine aqueous solutions ($[Ca]_0$=100.0 mg/L, Guinama 99.8%) were studied in a photocatalytic 1.0 L reactor provided with an UV-150W mercury lamp of medium pressure (Heraeus, transmission between 300 and 570 nm). Reactions began adding the iron catalyst ($[Fe]_0$=0-30.0 mg/L, $FeSO_4$, 99.0%) and the oxidant dosage for each set of experiments, which varied between ($[H_2O_2]_0$=0-15.0 mM, 30%V). All experiments were conducted at 25.0°C and pH=3.0.

3. Results and Discussion

All the tests conducted confirm that the DO concentration in the oxidized water present kinetic evolutions according to the cycles described in Fig. 1a. A kinetic model is proposed for the changes of DO. The adjustments made (Fig. 1b) show that both the reaction stage where the oxygen evolution occurs (DO_f, mg/L) and the step where oxygen is consumed (DO_d, mg/L), adjust to zero order kinetics (Eqs 1-6). Furthermore, it is noted that the dosage of iron has its greatest effect in the reactions that cause oxygen formation (Eqs 7-8). Meanwhile, the result is lower in the stage of oxygen consumption (Eq. 9).

$$\frac{d\,[DO]}{dt} = k_f \quad \rfloor_{DO_0}^{DO_{max}} \tag{1}$$

$$-\frac{d\,[DO]}{dt} = k_d \quad \rfloor_{DO_{max}}^{DO_\infty} \tag{2}$$

The corresponding kinetic equations are obtained:

$$[DO]_f = [DO]_0 + k_f\ t \qquad (5)$$

$$[DO]_d = [DO]_{max} - k_d\ (t - t_{max}) \qquad (6)$$

$$[DO]_{max} = 1.93\,[Fe]_0 + 26.835 \qquad (7)$$

$$k_f = 29.48\,[Fe]_0^{-1.25} \qquad (8)$$

$$k_d = -0.006\,[Fe]_0^{2.0} + 0.244\,[Fe]_0 - 3.69 \qquad (9)$$

4. Conclusions

The concentration of DO increases linearly with the $[H_2O_2]_0$ used because the excess of oxidant decomposes to O_2. The rate of DO generation is closely related to the iron dose, obtaining the highest rates of O_2 generation when using $[Fe]_0$=10.0 mg/L. Once the DO reaches the maximum concentration, it decreases again as the hydrogen peroxide is exhausted.
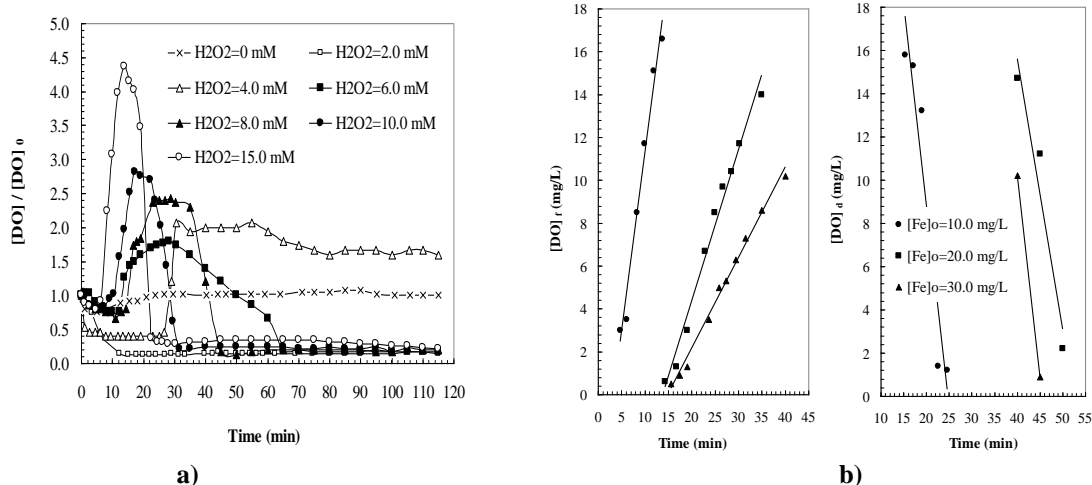

Figure 1. a) Effect of oxidant concentration on dissolved oxygen during the caffeine oxidation in a photo-Fenton system. Experimental conditions: $[Ca]_0$=100.0 mg/L; pH=3.0; $[Fe]_0$=10.0 mg/L; UV=150 W; T=25.0ºC. **b)** Estimation of zero-order kinetic constants for DO generation (k_f, mg/L min) and consumption of DO (k_d, mg/L min) during the caffeine oxidation. Experimental conditions: $[Ca]_0$=100.0 mg/L; pH=3.0; $[H_2O_2]_0$=15.0 mM; UV=150 W; T=25.0ºC.

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